EXPERIMENTS IN MOLECULAR OPTICS

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Abstract

A combined experimental and theoretical study of the manipulation of molecules with laser light is reported. It is shown that the dipole force produced by the electric field of a focused laser may be used to deflect, align, and orient molecules in a collision free environment. The feasibility of applying these techniques to nanolithography is explored, and a scheme for orienting molecules in space is developed.

I. Introduction

The broad objective of this research program is to use the dipole force of an electromagnetic field to control the motion of neutral atoms and molecules. In these studies, the intensity gradient of a focused laser beam serves as a "molecular lens" that can be used to deflect and focus a beam of particles. If, in addition, the molecules have an anisotropic polarizability, they may be aligned, or even oriented, by the field.

The potential energy induced by a far off-resonant field is given by

$$\mathcal{H} = -\frac{1}{4}\varepsilon^2(r)\left(\Delta\alpha\cos^2\theta + \alpha_\perp\right),$$

where $\vec{\varepsilon}(r)$ is the electric field, $\Delta\alpha = \alpha_{//} - \alpha_\perp$ is the polarizability anisotropy, $\alpha_{//}$ and $\alpha_\perp$ are the parallel and perpendicular components of the polarizability tensor, and θ is the angle between the principle axis of the molecule and the $\vec{\varepsilon}$ vector. If the atom or molecule is in its ground electronic state, the polarizability is positive and the potential energy is negative. In this case the particle experiences an attractive force that draws it into the field. A beam of such particles encountering a focused laser beam will therefore be focused or deflected by the molecular lens. If the molecule is anisotropic, the $\Delta\alpha\cos^2\theta$ term induces a torque that aligns the molecules. These effects provide the basis for several studies.

We report here five inter-related projects involving deflection and alignment of molecules and their reaction products. The first study investigates the anisotropic angular distributions of fragments obtained by photodissociation and photoionization of molecules with nanosecond lasers. The second project is the construction of an apparatus to measure the deflection of parent molecules by a focused laser field. The third project is a theoretical study of the application of molecular deflection to fabricate nanowires. The fourth project describes the construction of an apparatus designed to align molecules with femtosecond laser pulses. The final project is a theoretical investigation of the orientation of molecules by sequences of femtosecond laser pulses. We conclude with a list of publications resulting from this contract.

II. Anisotropic angular distribution of photodissociation and photoionization products obtained with nanosecond lasers

In this study we used the technique of velocity map imaging to measure the angular distributions of atoms, ions, and electrons produced in the photodissociation and photoionization of molecules by nanosecond lasers. In one experiment (paper 1) a 1064 nm Nd:YAG laser was used to align CH_3I molecules in a molecular beam, and a 306.47 nm dye laser was used to dissociate the molecules and detect the atomic iodine fragment. We found that the anisotropy of the iodine fragment could be controlled by varying the intensity of the IR laser and the delay between the two pulses. We interpreted these effects as caused by alignment of the parent molecule by the first laser. In a second series of experiments (papers 2-4) we discovered an unusual hourglass-shaped spatial distribution of the fragments of molecules (I_2, ICl, and iodobenzene) excited with visible and ultraviolet nanosecond lasers. We interpreted the data in terms of a three-body dissociative ionization process, in which a rapidly escaping electron carries off most of the energy. The anisotropy of the fragments is caused by selective excitation of aligned molecules.

III. Construction of a molecular beam deflection apparatus

A molecular beam apparatus shown schematically in Fig. 1 was constructed. Counter-propagating IR and UV laser beams intersect a pulsed molecular beam. The first laser deflects the beam, and the second ionizes the parent molecule, which is detected by velocity map imaging. A novel feature is an Einzel lens, which magnifies the deflection of the ions. Initial results of the deflection of carbon disulfide are displayed in Fig. 2.

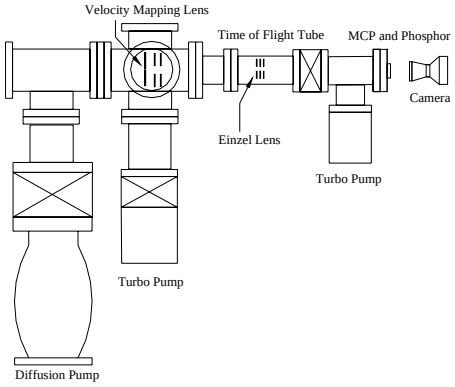

Figure 1. Schematic drawing of molecular beam deflection apparatus.

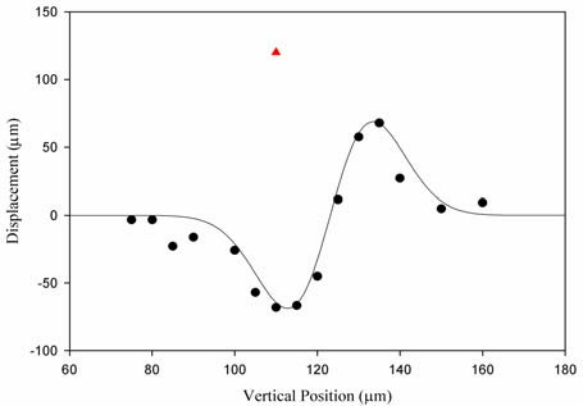

Figure 2. Deflection of CS_2 molecules.

IV. Theoretical study of nanolithography with molecular optics

A technologically useful application of molecular optics is the creation of nanostructues by focusing a molecular beam of neutral molecules onto a surface. We have performed a detailed theoretical study of the feasibility of creating nanowires by this technique (paper 5). We showed that a grazing angle of incidence between the laser and molecular beams reduces the component of the kinetic energy transverse to the laser beam, allowing a proportionate reduction in laser intensity, while preserving the focal length of the molecular beam. A resulting reduction in the required laser intensity allows one to use a continuous-wave laser to form very long nanostructures. A further order of magnitude reduction in requisite power may be achieved by intersecting the laser and molecular beams inside the laser cavity. We further showed that the focal coordinates, (x_f, z_f), of the molecular lens and the width, W, of the nanowire scale as

$$x_f, z_f \sim m\omega_0 T_0 / m_c \alpha_{//} I_0$$

$$W \sim W_i / \omega_0^2,$$

where m and m_c are the masses of the deposited molecule and the carrier gas, respectively, T_0 and W_i are the stagnation temperature and initial width of the molecular beam, and ω_0 and I_0 are the 1/e radii of the field and peak intensity of the laser beam. A representative calculation shows that nanowires 50 nm wide and 100 μm long may be deposited with a 100 W Yb:YAG thin-disk laser. Some results of the study are shown in Fig. 3.

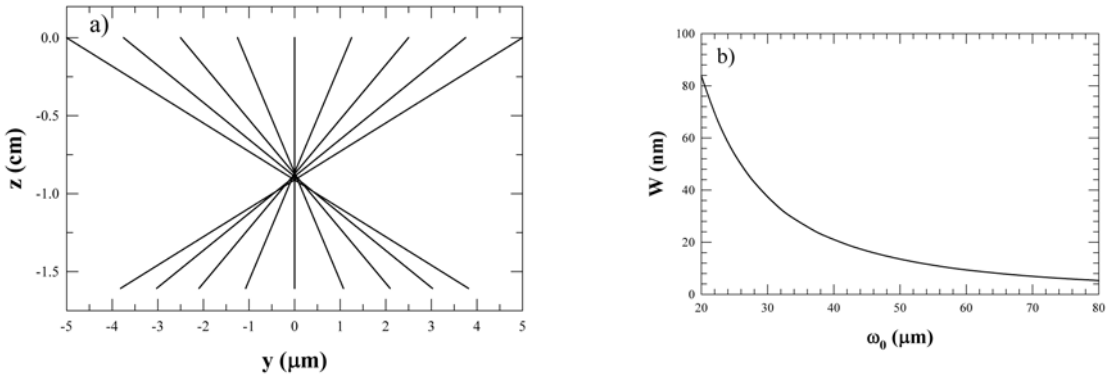

Figure 3. The effect of spherical aberration on the focal width of the molecular beam. (a) Trajectories for a molecular beam of I_2 in Kr having an initial width $W_i = 10\mu m$ focused by a laser with $\omega_0 = 30\ \mu m$, at a peak intensity of 10^8 W/cm^2 and an intersection angle of 5^0. Both the translational and rotational temperatures are zero. (b) Variation of the focal width with the radius of a circular Gaussian focus.

V. Alignment of molecules with femtosecond laser pulses

Molecules irradiated with an intense ultrashort laser pulse undergo a series of Raman transitions that produce rotational wave packets aligned along the direction of the electric field vector. These wave packets have a long-term coherence and display a recurrence of their alignment, with a revival time of $(2Bc)^{-1}$, where B is the rotational constant and c is the speed of light. Such revivals are important because they allow one to produce aligned molecules under field-free conditions.

To study this effect we modified an existing molecular beam apparatus equipped with a photofragment imaging detector. A newly acquired Ti:Sapppire laser was used to align iodine molecules, and preliminary results displayed rotational revivals.

VI. Orientation of molecules with femtosecond pulses

Alignment and anti-alignment conventionally refer to head-on vs. broadside localization of the symmetry axis of a molecule, whereas orientation refers to control of the up and down directions of an aligned molecule. In this project we explored the role of laser induced anti-alignment in enhancing molecular orientation (papers 6-7). A technique for obtaining field-free orientation via anti-alignment was developed, which combines a linearly polarized femtosecond laser pulse with a half-cycle pulse. The laser pulse induces transient anti-alignment in the plane orthogonal to the field polarization, while the half-cycle pulse causes the orientation. We identified two qualitatively different enhancement mechanisms that depend on the pulse order, and optimized their effects using classical and quantum models both at zero and non-zero temperature.

VII. Publications resulting from this contract

1. A. Sugita, M. Mashino, M. Kawasaki, Y. Matsumi, R. J. Gordon, and R. Bersohn, "Control of Photofragment Velocity Anisotropy by Optical Alignment of CH_3I," J. Chem. Phys. **112**, 2164 (2000).

2. H. Yamada, N. Taniguchi, M. Kawasaki, Y. Matsumi, and R. J. Gordon," Dissociative Ionization of ICl Studied by Ion Imaging Spectroscopy," J. Chem. Phys. **117**, 1130 (2002).

3. S. Unny, Y. Du, L. Zhu, R. J. Gordon, A. Sugita, M. Kawasaki,Y. Matsumi, and T. Seideman, "Above-Threshold Dissociative Ionization in the Intermediate Intensity Regime," Phys. Rev. Lett**.** **86**, 2245 (2001).

4. S. Unny, Y. Du, L. Zhu, K. Truhins, R. J. Gordon, A. Sugita, M. Kawasaki, Y. Matsumi, R. Delmdahl, D. H. Parker, and A. Berces, "Above-Threshold Effects in the Photodissociation and Photoionization of Iodobenzene," J. Phys. Chem. A **105**, 2270 (2001).

5. R. J. Gordon, L. Zhu, W. A. Schroeder, and T. Seideman, "Nanolithography Using Molecular Optics," J. Appl. Phys. **94**, 669 (2003).

6. E. Gershnabel, I. Sh. Averbukh, and R. J. Gordon, "Enhanced Molecular Orientation Induced by Molecular Anti-Alignment," Phys. Rev. A **74,** 053414, 2006.

7. E. Gershnabel, I. Sh. Averbukh, and R. J. Gordon, "Orientation of Molecules via Laser-Induced Antialignment," Phys. Rev. A **73,** 061401(R), 2006.